

UK Patent Application (12) GB (19) 2 322 137 (13) A

(43) Date of A Publication 19.08.1998

(21) Application No 9703095.1	(51) INT CL ⁶ C11D 3/37 // C08B 31/00, C08F 251/00 (C11D 3/22 3:37)
(22) Date of Filing 14.02.1997	
(71) Applicant(s) Unilever Plc (Incorporated in the United Kingdom) Unilever House, Blackfriars, LONDON, EC4P 4BQ, United Kingdom	(52) UK CL (Edition P) C5D DHC D107 D108 D110 D111 D131 D142 D153 D180 C3P PFC P322 P330 P368 P370 P372 P380 C3U UDC UDE U311 U319
(72) Inventor(s) Perincheery Aravindakshan Velasudhan Nair Gopa Kumar Anuradha Moulee	(56) Documents Cited GB 2277325 A GB 2063282 A GB 1588688 A EP 0703243 A1 EP 0663969 A1 EP 0603837 A1 WO 95/33894 A1 WO 95/33813 A1 WO 95/30731 A1 WO 93/11214 A1 DE 019532542 A1 DE 002806450 A US 5227448 A US 5223171 A US 4465618 A Derwent Abstract No.95-128487/199517 relating to JP00053774 (Chisso) 28.02.95 Derwent Abstract No.81-08817D/198106 relating to JP550155097 (Nichiden) 03.12.80
(74) Agent and/or Address for Service Peter G Mole Unilever Plc, Patent Division, Colworth House, Shambrook, BEDFORD, MK44 1LQ, United Kingdom	(58) Field of Search UK CL (Edition O) C3P PFC, C3U UDC UDE, C5D DEX INT CL ⁶ C08B, C08F, C11D Online: WPI

(54) Abstract Title
Detergent composition with soil release agents

(57) Soil release agents for use in fabric washing detergent compositions are provided in which hydrophilic polysaccharide such as starch is modified to impart soil release properties. The modification required leads to the inclusion of hydrophobic or hydrophilic moieties giving soil release benefits.

The starch may be reacted with an anhydride, copolymerised with an acrylate or vinyl acetate, or with hydrophobic cationic moieties.

The detergent composition may include linear alkyl benzene sulphonate, sodium tripolyphosphate, soda, sodium silicate, and sodium sulphate.

GB 2 322 137 A

DETERGENT COMPOSITION WITH SOIL RELEASE AGENTS

The present invention relates to synergistic detergent formulations containing soil release agents/polymers for use in the removal of oily soils from fabrics.

Difficult removal of oily soil has been a problem associated with the use of polyester fibers. Since the mid 60's it is known to provide such fibers with textile finishes to improve oily soil repellency. These finishes usually combine hydrophobic and hydrophilic moieties. A variety of chemical structures have been evaluated for such finishes. Broadly, essential requirements of such polymers are to have high molecular weight, to be chemically linked to the fabric and be readily wettable in an aqueous environment.

The thrust in recent times has been the development of polymers which can be incorporated into detergent formulations to provide soil release benefits during washing processes. The polymers suitable for the purpose are identified as low molecular weight polymers for easy dissolution or dispersion in a surfactant solution and exhibiting substantivity to the fibre from a detergent solution. Additionally the polymer should be compatible with the components of the detergent formulation. Polymers containing hydrophobic and hydrophilic moieties are known for such use wherein the hydrophobic segment is usually poly (ethylene terephthalate) (PET) while the hydrophilic segment is typically a polyether, usually poly ethylene glycol (PEG).

US 3,416,952 (1968) relates to the modification of polyester articles (fabric, film, powder) and the use of poly(ethylene terephthalate) (PET), poly(oxyethylene terephthalate) (POET) copolymers as soil release textile finishes.

EP 0 815 427 (1986) relates to the inclusion of PET:POET copolymers in detergent formulations. Oxyethylene groups can be partially substituted with oxypropylene groups. Benefits are greatest when nonionic surfactants are used.

US 4,999,128 (1991) reports PET:POET copolymers where part of the ethylene terephthalate units are replaced by ethylene isophthalate units and the resulting copolymers are effective soil release agents.

WO 94/03570 (1994) shows that inclusion of sulphonated terephthalate units in the copolymer gives enhanced water solubility and superior soil release properties.

EP 0311 342 (1989) indicates that the presence of sulfaroyl end groups also gives enhanced soil release properties.

WO 95/02028 (1995) shows that incorporation of sulphonated poly(ethoxy) or poly(propoxy) units in the PET:POET copolymer as end groups shows enhanced water solubility and soil release properties. The materials are cheaper than PET:POET copolymers with

sulphonated aryl groups.

The polymers reported in the prior art tend to undergo hydrolysis in detergent formulations and thus have a poor stability under alkaline conditions. The estimated cost to performance ratio is high.

The polymers of the present invention, due to the starch backbone will have greater biodegradability, show stability in the detergent formulations in comparison to the synthetic soil release polymers reported in the prior art and also have good soil release properties. The products are also expected to have improved cost to performance ratio.

It is the basic objective of the present invention to provide for soil release polymers which are made from a readily available renewable resource, an example of which is starch, suitable for use with detergent formulations.

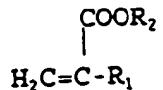
A further object of the present invention is to provide synergistic detergent formulations incorporating soil release polymers which would be effective in the removal of oily soils from polyester and blended polyester-cotton.

Thus according to one aspect of the present invention, a hydrophilic polysaccharide, such as starch, is modified to impart

desirable attributes like soil release performance. In particular, the invention provides for three different methods of starch modifications which are as follows:-

i) Reaction of starch hydroxyls with C_2 - C_6 dianhydride substituted with a C_5 - C_{12} alkyl/alkenyl side group wherein the degree of substitution is 1-3.

ii) Graft copolymerisation of hydrophobic acrylate monomer or vinyl acetate on starch, wherein the synthetic polymer content is 1-15% with respect to starch. The structure of acrylate monomers is as follows, wherein R_2 is an alkyl group (C_1 - C_3), preferably methyl. R_1 is preferably H but can also be an alkyl group.



iii) Reaction with hydrophobic cationic moieties like hydroxypropyl dodecyldimethyl ammonium chloride with possible further enhanced hydrophilicity by graft copolymerisation with water soluble acrylic monomer an e.g. of which is methacrylic acid.

According to another aspect of the present invention synergistic detergent formulations are provided incorporating the modified starch polymer such as herein described to thereby improve upon the detergency characteristics of the detergent especially with

regard to removal of oily soil from fabrics.

The detergent formulations of the invention also contain, as in conventional formulations, detergent-active compounds (surfactants) and detergency builders, and may also contain fillers, minor ingredients, such as colour, perfumes, enzymes, fluorescers, brighteners, anti redeposition agents, bleaches as desired.

The detergent active compound may be anionic, nonionic, cationic, zwitterionic, or mixtures thereof, as well known to those skilled in the art and generally described in literature, for example in *Surface Active Agents and Detergents, Volume II* by Schwartz, Perry and Berch (Interscience Publishers, N.Y. 1958).

Especially preferred are compositions in which the surfactant is anionic. Suitable anionic actives which may include linear alkyl benzene sulphonates (LAS) of formula $R-C_6H_4-SO_3M$ and primary alkyl sulphates of formula $ROSO_3M$ wherein R is a linear or branched primary alkyl or alkenyl group containing 8 to 22 carbon atoms, preferably 10 to 18 carbon atoms and M is a cation such that the detergent active is water soluble.

Other anionic actives which may be employed, preferably in an amount less than that of primary alkyl sulphate (PAS) and/or LAS, may for example, be selected from alkyl sulphonates, secondary alkyl sulphates, olefin sulphonates, fatty acid ester sulphonates,

alkyl ether sulphates and combination thereof.

Especially preferred are compositions in which the anionic detergent active comprises of alkyl benzene sulphonate (LAS). The detergent component may be 2-95%, preferably 5-30%, by weight of the complete composition.

The detergency builders used in the formulation are preferably inorganic and suitable builders, for example, alkali metal aluminosilicates (zeolites), sodium carbonate, sodium tripolyphosphate (STPP), tetrasodium pyrophosphate (TSPP), and combinations of these. Builders are suitably used in an amount ranging from 1 to 50 wt%, preferably from 5 to 30 wt% by weight of the complete composition.

Fillers suitable for use in the formulation include kaolin, calcite, talc, soapstone, china clay and the like, used singly or in combination, suitably in an amount ranging from 10 to 75 wt% by weight, preferably from 20 to 40 wt%.

Minor components such as perfumes, colouring agents, fluorescers, enzymes, anti redeposition agents, bleaches and the like can also be used, for example, in an amount of up to 10 wt%.

The modified starch polymer is incorporated at a level of 0.01-10% by weight of the detergent formulation, preferably 0.5-2%.

It is thus possible by way of this invention to provide modified starch polymers that incorporate both hydrophobic and hydrophilic moieties, having soil release benefits. The invention thus further provides for the formulation of detergents incorporating the modified starch/polymer to achieve improved detergency and oily soil removal properties in detergents.

The nature of the invention, its objects and advantages will be more apparent from the ensuing description made with relation to non-limiting exemplary illustrations of the above identified various aspects of the present invention.

EXAMPLES:

1. SYNTHESIS OF MODIFIED STARCH/POLYMERS OF THE INVENTION.

EXAMPLE : A

Synthesis of octenyl succinic anhydride (OSA) derivative of starch
1 kg of tapioca starch was slurried in 1.5 liter of water. 30 g of octenyl succinic anhydride (OSA) was added to it under good agitation. The pH was adjusted to 7.5-7.7 and the mixture stirred at room temperature for 20 hrs. while maintaining the pH between 7.5 and 7.7. The pH was then adjusted to 5 with 3N HCl. The reaction mass was then filtered, washed three times with water and dried in air. This was followed by oven drying at 50°C till the moisture content was 10% by weight.

The OSA content was estimated by determining the free acid groups

(by acid-base titration) to determine the level of starch modification. The % add on of OSA by weight was 1.95.

EXAMPLE : B

Synthesis of starch-graft-poly(methyl acrylate)

10g urea was dissolved in 250 ml. of distilled water and placed in a 3-necked round bottomed flask equipped with a stirrer and thermometer pocket. 100 gms. of tapioca starch was then added to it and the mixture stirred for one hour. Solutions of ferrous ammonium sulphate (0.2 g in 10 ml. distilled water), ascorbic acid (1g in 10 ml. water) were then added. This was followed by addition of 10 ml. of methyl acrylate and the mixture was then stirred for five minutes. 1ml of hydrogen peroxide (30% W/V) was then added and the mixture stirred for two hours. At the end of this period the contents of the flask were filtered, washed repeatedly with 2 liters of distilled water and then air dried. The product was finally dried at 120°C for 5-6 hrs. The product was used as such for soil release evaluation.

EXAMPLE : C

Synthesis of starch-graft-poly(vinyl acetate)

5 g zinc chloride was dissolved in 100ml distilled water. 50 gms tapioca starch is slurried in this solution and the whole mixture stirred for one hour. At the end of this period ascorbic acid solution (0.5 g in 10 ml) was added to the mixture followed by addition of 10 ml vinyl acetate monomer over 5 min. interval. The

mixture was then stirred for 10 mins. followed by addition of 1 ml hydrogen peroxide (30% W/V). The stirring is then continued for 2 hours. At the end of this period 200 ml water was added and the reaction mixture filtered followed by washing repeatedly with water. The mixture was then air dried followed by drying in the oven at 110°C for 8 hrs.

EXAMPLE : D

Synthesis of cationic starch-graft-poly(methacrylic acid)

500 gms of tapioca starch was slurried in 500 ml of water. 15 g urea was then added and the reaction mass stirred for 30 mins. 0.5 g ferrous ammonium sulphate, followed by 2.5 g ascorbic acid and 50 g methacrylic acid were added to it. After 10 minutes, 5 ml hydrogen peroxide (30% w/v) was added. Subsequently, 125g sodium sulphate and 25g sodium carbonate were added to it. The pH was then adjusted to 11.5 with 3% sodium hydroxide and 37.5g hydroxypropyl dodecyldimethyl ammonium chloride(HDAC) was then added. The pH was maintained at 11.5-11.8 by addition of 3% sodium hydroxide solution and the reaction was continued for 16 hours at 40° C. The pH was then adjusted to 5.8 and the material filtered, washed and dried.

The methacrylic acid content is estimated by determining the acid value as in example A and was 5.96%. The HDAC content was determined by estimating the nitrogen content in the modified starch by Kjeldahl's method and was found to be 3.11%.

The characteristics of the above produced starch based soil release polymers of Examples A to D obtained in accordance with the present invention are detailed in TABLE I hereunder:

TABLE I

Example (starch)	Hydrophilic moiety	Hydrophobic moiety	% hydrophobic modification
Example A	Starch	Octenyl succinic anhydride	1.95
Example B	Starch	Poly(methyl acrylate)	3.6
Example C	Starch	Poly(vinyl acetate)	5.8
Example D	Starch graft PMAA	hydroxypropyl dodecyldimethyl ammonium chloride (HDAC)	3.11

2. DETERMINATION OF SOIL REMOVAL:

The composition of the detergent formulation used in the study is given below.

Detergent formulation:

The detergent composition used in the study contained the following major components:

linear alkyl benzene sulphonate	20%
sodium tripoly phosphate	27%
Soda	10%
Silicate	10%
Sodium Sulphate	18.5%

The test fabric:

Swatches made of 100% polyester fabric, were of dimension 5" x 5" (approx. weight 1g.).

The soil release polymers:

The test polymers (examples A to D) or a standard PET-POET copolymer type soil release polymer e.g. Permalose was incorporated at 2% by weight into the detergent formulation described above.

Wash Conditions:

The detergent concentration used in the wash liquor was 5g/liter and the fabric was washed using water of hardness 5°FH. A cloth to wash liquor ratio of 1 : 30 ml. was maintained. The cloth to rinse liquor was 1 : 200 ml. 10 replicates were used for each polymer to be tested.

Soils

The soils used were triolein, artificial sebum and motor oil. The artificial sebum was prepared as follows:

Coconut oil, Coconut oil fatty acid (CNFA), lanolin and mineral oil were mixed in the following proportions.

Coconut Oil	9 parts
CNFA	4.5 parts
Lanolin	0.97 parts
Refined mineral oil	1.87 parts

Oil Red dye was incorporated in all soils at 0.025% levels.

a) Oily soil removal.

The evaluation consists of four steps: desizing, pre-treatment of the fabric, soil loading and testing of soil release.

Desizing:

Fabrics were desized by washing in a 5% solution of the detergent in the washing machine for 1 hour. This procedure was repeated thrice and the fabric was then rinsed and dried.

Pretreatment of the fabric :

The pretreatment of the fabric was carried out in a tergo-to-meter by agitating the fabric pieces in the detergent solution with and without the soil release polymers for a period of 15 minutes under the wash conditions described above. After rinsing, the test pieces were air dried, followed by oven drying at 80-90°C.

Soil loading:

0.2g of soil along with oil red dye at a concentration of 0.025% was loaded on to each of the test swatches and the stain was allowed to wick for a period of 17 hrs. Initial reflectance measurement at 520nm was taken, on a Milton Roy Color Scan II. R520 is the wavelength at which the red dye absorbs, hence it is used to monitor soil removal.

Testing of soil release:

The test swatches were then washed in a tergo-to-meter in the detergent solution with and without the soil release polymers (Examples A to D) for a period of 15 minutes under the wash conditions described above. Commercially available soil release polymer Permalose was maintained for comparison. Reflectance

measurements were taken at 520nm. The difference in reflectance of the stained fabrics before and after washing was noted and represented as $\Delta R520^*$.

The results of the tergo-to-meter washes using detergent solution with and without the soil release polymers following the above soil release test procedure for removal of oily soils is reported in Table II.

Improvement in oily soil removal ($\Delta \Delta R520^*$) =

$\Delta R520^*$ (for detergent containing soil release polymer) - $\Delta R520^*$ (for detergent without soil release polymer).

Polymer used	Triolein	Artificial Sebum	Motor Oil
	$\Delta \Delta R520^*$	$\Delta \Delta R520^*$	$\Delta \Delta R520^*$
Permalose	no benefit	1.5	3.5
Example A	0.8	1.9	2.7
Example B	1.3	1.9	3
Example C	0.7	no benefit	5.5
Example D	1.5	3	3.4

The above reflectance measurement of $\Delta \Delta R520^*$ values indicate benefits in use of modified starch based polymers in removal of oily soil.

b) Composite (oily and particulate) soil removal:

WFK fabric swatches (3" x 3"), presoiled with carbon soot and artificial sebum, was used to evaluate detergency when soil release polymers are incorporated in the detergent. WFK 30D (polyester) and WFK 20D (polycotton) (supplied by Global Resources Management Centre, Madras) was used in these studies. Initial reflectance measurements at 460nm (R460*) were recorded. The swatches were subjected to a wash cycle following the procedure described earlier. The difference before and after washing is noted and represented as $\Delta R460^*$. Improvement in soil removal ($\Delta \Delta R460^*$) = $\Delta R460^*$ for detergent + polymer - $\Delta R460^*$ for detergent. The data are presented in Table III.

Table III

Test Polymer	$\Delta \Delta R460^*$ (WFK 30D)	$\Delta \Delta R460^*$ (WFK 20D)
Permalose	1.6	no benefit
Example A	2.5	2.1
Example B	2.7	no benefit
Example C	2.6	1.1
Example D	1.0	1.0

The above disclosure thus provides for new generation of soil release polymer based on hydrophobic modification of starch and also provides for synergistic combination of such modified starch/polymer with detergents to thereby improve upon the detergency characteristics of detergents and importantly as far as oily soil removal from polyester fabrics are concerned.

CLAIMS:

1. A method of producing a soil release agent for use in a fabric washing detergent composition, comprising modifying a hydrophilic polysaccharide.
2. The method according to claim 1, wherein the hydrophilic polysaccharide comprises starch and the modification comprises the steps of reacting the starch with C₂-C₆ dianhydride substituted with a C5 - C12 alkyl or alkenyl side group, the degree of substitution being in the range 1-3.
3. The method according to claim 1, wherein the hydrophilic polysaccharide comprises starch and the modification comprises the step of graft copolymerisation of hydrophobic acrylate monomer or vinyl acetate onto the starch, the weight ratio of synthetic polymer to starch being in the range of 1-15%.
4. The method according to claim 1, wherein the hydrophilic polysaccharide comprises starch, the modification including the steps of reaction with hydrophobic cationic moieties and, optionally, graft copolymerisation with water soluble acrylic monomer.
5. Soil release agent produced by the method of any of the preceding claims.
6. A fabric washing detergent composition comprising detergent active, detergency builder and soil release agent according to claim 5.



Application : GB 9703095.1
Claims searched: 3

Examiner: Michael Conlon
Date of search: 17 September 1997

Patents Act 1977
Further Search Report under Section 17

Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

UK Cl (Ed.O): C3P (PFC) C5D (DEX)

Int Cl (Ed.6): C08F, C11D

Other: Online: WPI

Documents considered to be relevant:

Category	Identity of document and relevant passage	Relevant to claims
X	GB1568688 (Stadex) Example 23	3
X	WO95/33894 A1 (Unilever)	3
X	WO95/33813 A1 (Unilever)	3
X	EP0663969 A1 (BASF)	3
X	DE19532542 A1 (Henkel) claim 1	3
X	Derwent Abstract No.95-128487/199517 relating to JP700053774 (Chisso) 28.02.95	3
X	Derwent Abstract No. 81-08817D/198106 relating to JP550155097 (Nichiden) 03.12.80	3

X	Document indicating lack of novelty or inventive step	A	Document indicating technological background and/or state of the art.
Y	Document indicating lack of inventive step if combined with one or more other documents of same category.	P	Document published on or after the declared priority date but before the filing date of this invention.
&	Member of the same patent family	E	Patent document published on or after, but with priority date earlier than, the filing date of this application.



The
Patent
Office

18

Application No: GB 9703095.1
Claims searched: 4

Examiner: Michael Conlon
Date of search: 17 September 1997

Patents Act 1977
Further Search Report under Section 17

Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

UK Cl (Ed.O): C3U (UDE) C5D (DEX)

Int Cl (Ed.6): C08B, C11D

Other: Online: WPI

Documents considered to be relevant:

Category	Identity of document and relevant passage	Relevant to claims
A	GB2277325 A (Unilever)	4
A	GB2063282 A (Roquette)	4
A	DE2806450 A (Hoffman)	4

X Document indicating lack of novelty or inventive step
Y Document indicating lack of inventive step if combined with one or more other documents of same category.
& Member of the same patent family

A Document indicating technological background and/or state of the art.
P Document published on or after the declared priority date but before the filing date of this invention.
E Patent document published on or after, but with priority date earlier than, the filing date of this application.



The
Patent
Office

19

Application No: GB 9703095.1
Claims searched: 1 and 2

Examiner: Michael Conlon
Date of search: 14 May 1997

Patents Act 1977
Search Report under Section 17

Databases searched:

UK Patent Office collections, including GB, EP, WO & US patent specifications, in:

UK Cl (Ed.O): C3U C5D

Int Cl (Ed.6): C11D C08B

Other: Online: WPI

Documents considered to be relevant:

Category	Identity of document and relevant passage	Relevant to claims
X	EP0703243 A1 (Unilever) the Example	1 and 2
X	EP0603837 A1 (National Starch) page 3 lines 21 to 33	1 and 2
X	WO95/30731 A1 (BASF) Polymer 1 on page 14	1 and 2
X	WO93/11214 A1 (BASF) page 7 line 36ff	1
X	US5227446 (BASF) Example 11	1 and 2
X	US5223171 (Rhone Poulenc) Example 1	1
X	US4465619 (Lever Brothers) Example 1	1 and 2

X Document indicating lack of novelty or inventive step	A Document indicating technological background and/or state of the art.
Y Document indicating lack of inventive step if combined with one or more other documents of same category.	P Document published on or after the declared priority date but before the filing date of this invention.
& Member of the same patent family	E Patent document published on or after, but with priority date earlier than, the filing date of this application.